Spontaneous magnetic order in random dipolar solids

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Randomly positioned dipoles tend to align at low temperatures due to interactions with a mean field. Random dipolar positions lead to fluctuations which can inhibit ordering, even at $T=0$. We show fluctuations dominate the mean field at low densities of dipoles, preventing order at any temperature. At high densities, in contrast, the mean field dominates and ordering is possible.

I. INTRODUCTION

Randomly positioned dipolar solids arise in many contexts and offer the possibility of important applications. In partially occupied crystal lattices of $LiHo_xY_{1-x}F_4$, randomly positioned magnetic holmium ions interact primarily through their dipoles.[1] Giant magnetoresistance materials[2] place magnetic cobalt or iron nanocrystals within a pure copper environment. Room-temperature transparent ferromagnets[3] consisting of magnetite nanocrystals in a polymer matrix hold promise as a component in inks for printers. Dipole interactions may influence magnetic properties of cobalt- or gadolinium-filled Bucky onions[4] embedded in an amorphous carbon soot. Ferrofluid, a coloidal suspension of magnetic grains in a liquid solvent, may be cooled below the solvent freezing temperatures.[5] Likewise, electric[6,7] dipoles may occupy random positions.

Two characteristics of dipoles lead to unusual difficulties in analyzing these systems: long range and anisotropy. The field at point $\mathbf{r}=r\hat{r}$ due to a dipole moment μ at the origin is

$$\mathbf{H}(\mathbf{r})=\frac{3\hat{r}(\mu\cdot\hat{r})-\mu}{r^3} . \tag{1}$$

The r^{-3} falloff leads to conditional convergence of the local field due to a distribution of dipoles at remote locations. With proper treatment of boundary effects[8] that problem may be resolved. The anisotropy leads to frustration in aligning favorably with nearby dipoles. We believe a dipolar glass state arises as a result of such frustration.[9]

Conventional mean-field theory[8,10,11] predicts a dipole system spontaneously magnetizes at a critical temperature T which is proportional to the density of dipoles. Consequently, the system is ferromagnetic for any density at $T=0$. However, Luttinger and Tisza[12] prove that at zero temperature, dipoles on a face- or body-centered-cubic lattice order ferromagnetically while those on a simple-cubic lattice order antiferromagnetically. In other words, orientational order in a dipole system depends on the positional arrangements of the dipoles. The absence of ferromagnetic order in frozen ferrofluids[5] consisting of randomly positioned dipoles also suggests the need to refine conventional mean field theory. This paper focus on the effect of random dipole positions on spontaneous magnetic order. Random positions induce local field fluctuations,[13] which tend to suppress magnetic order.[7] Unlike thermal fluctuations, which vanish at zero temperature, local fluctuations arising from positional randomness prevent magnetic order in dilute dipole systems even at $T=0$.[7,14]

Klein *et al.*[6] pioneered a self-consistent theory of randomly positioned point dipoles to study polar impurities on randomly chosen lattice sites. Vugmeister and Glinchuk[7] employed this theory to study orientational ordering in randomly positioned point dipoles. They concluded that local field fluctuations due to positional randomness prevent the emergence of long-range orientational order even at $T=0$. We note that the closeness of neighboring dipoles is limited by the hard-sphere diameter in the case of ferrofluids and by the lattice constant in the case of lattice impurities. Since the dipole-dipole interaction diverges rapidly at zero distance, neglecting this minimum separation greatly exaggerates local fluctuations due to positional randomness and alters the qualitative behavior of the system.

Two key dimensionless parameters characterize a system of dipolar hard spheres. For sphere diameter a, we define the volume fraction

$$\phi\equiv\frac{\pi}{6}\rho a^3 , \tag{2}$$

which is a dimensionless measure of density. The dimensionless reduced temperature

$$T^*\equiv\frac{k_BTa^3}{\mu^2} \tag{3}$$

reflects the thermal energy as a fraction of dipole energy at contact.

Magnetic interactions depend on relative positions of the dipole moments. The complete pair correlation function in a dipole system can be expanded in the form

$$g(\mathbf{r},\mu_1,\mu_2)=\sum_{mnl} g^{mnl}(r)\Phi^{mnl}(\hat{r},\hat{\mu}_1,\hat{\mu}_2) , \tag{4}$$

where $\hat{\mu}_i$ are the orientations of their dipole moments μ_1, $\hat{r}$ is the orientation of their separation $\mathbf{r}$, and $\Phi^{mnl}(\hat{r},\hat{\mu}_1,\hat{\mu}_2)$ are orientational invariants.[17–19] The projection $g^{000}(r)$ is the usual radial distribution function. Both conventional and generalized mean-field theories

decouple orientational and spatial degrees of freedom, and use the positional correlation function $g(\mathbf{r})$. We consider a fixed, random, distribution of particles and set the positional correlation function $g(\mathbf{r})=g^{000}(r)=1$ outside the hard-sphere diameter. This approximation is reasonable for the frozen ferrofluid experiments and very dilute dipolar defects occupying randomly chosen sites of a regular lattice.

Each type of these randomly positioned dipole systems has its own peculiarities relevant to magnetic order. Dipolar defects on a lattice assume discrete dipole orientations dictated by the crystal field. Uniaxial anisotropy restricts moments to $\pm\hat{z}$ directions. We call these Ising dipoles.[1,7] In frozen ferrofluid, the frozen solvent immobilizes the dipolar particles, but imposes no field to influence dipole orientations. In many cases, the dipole moment of a particle rotates freely, even though the particle itself is held rigidly. However, each magnetic particle may have an easy axis[5] created by a combination of crystal fields and a spherical particle shape. The magnetic moment of a particle prefers to point along the easy axis to lower energy, as in the case of Ising dipoles. These easy axes are locked in random orientations since the particles cannot rotate. We therefore call these particles random axis Ising dipoles.

This paper first reviews conventional mean-field theory, then Klein's generalization to include local fluctuations. We then apply the generalized theory, successively, to freely rotating dipoles, Ising dipoles, and random axis Ising dipoles. Preliminary results for freely rotating dipoles are reported in an earlier paper.[14]

II. CONVENTIONAL MEAN FIELD THEORY

In conventional mean-field theory, each dipole $\boldsymbol{\mu}_i$ feels a mean field $\mathbf{H}_0$ which is identical for all dipoles. This mean field $\mathbf{H}_0$ determines the thermal average of $\boldsymbol{\mu}_i$ at site i:

$$\langle \boldsymbol{\mu}_i \rangle_T = \frac{\sum_{\boldsymbol{\mu}} \boldsymbol{\mu} e^{\beta \boldsymbol{\mu}\cdot\mathbf{H}_0}}{\sum_{\boldsymbol{\mu}} e^{\beta \boldsymbol{\mu}\cdot\mathbf{H}_0}} , \tag{5}$$

which is also identical for all dipoles. The subscript T indicates a thermal average. We define the magnetic order parameter as the magnetization per unit volume,

$$\mathbf{M} \equiv \rho \langle \boldsymbol{\mu} \rangle_T , \tag{6}$$

where ρ is the dipole number density. Treating the system as a continuum, we obtain the mean field $\mathbf{H}_0$ as a function of the order parameter $\mathbf{M}$,

$$\mathbf{H}_0 = \int d^3\mathbf{r}\, g(\mathbf{r}) \frac{3\hat{r}(\mathbf{M}\cdot\hat{r})-\mathbf{M}}{r^3} = \frac{4\pi}{3}\mathbf{M} . \tag{7}$$

The integral is calculated for positional correlation function

$$g(\mathbf{r}) = \begin{cases} 1 & \text{if } r > a , \\ 0 & \text{if } r < a \end{cases} \tag{8}$$

contained within an infinitely prolate spheriod[8] with major axis in the direction of magnetic order $\mathbf{M}$.

Equations (6) and (7) constitute a self-consistent mean-field theory. $H_0 = M = 0$ always solves the equation. Spontaneous order emerges when a nonzero solution for M and H_0 bifurcates from the zero solution. For the phase boundary of a continuous phase transition, we need only to examine the limit of weak mean field $\mathbf{H}_0$ and small order parameter $\mathbf{M}$. Expanding Eq. (5) for weak field H_0, Eq. (6) gives

$$M = \rho\beta H_0 \langle (\boldsymbol{\mu}\cdot\hat{z})^2 \rangle_{\hat{\mu}} , \tag{9}$$

where the average is performed over all allowed $\hat{\mu}$, and $\hat{z}$ is unit vector in the direction of both $\mathbf{M}$ and $\mathbf{H}_0$.

For Ising dipoles, $\boldsymbol{\mu}$ is confined in the $\pm\hat{z}$ directions, so Eq. (9) gives the order parameter in terms of the mean field

$$M = \rho\beta\mu^2 H_0 , \tag{10}$$

which along with Eq. (7) for the mean field in terms of the order parameter gives the phase boundary

$$\frac{4\pi}{3}\rho\beta\mu^2 = 1 . \tag{11}$$

The continuous magnetization phase boundary in the $\phi - T^*$ plane is therefore

$$T^* = 8\phi . \tag{12}$$

For freely rotating dipoles and random axis Ising dipoles, $\hat{\mu}$ points in all directions with equal probably. As a result, Eq. (9) for the order parameter gives

$$M = \tfrac{1}{3}\rho\beta\mu^2 H_0 , \tag{13}$$

which yields the continuous magnetization phase boundary in the $\phi - T^*$ plane,

$$T^* = \tfrac{8}{3}\phi . \tag{14}$$

As expected, Ising dipoles magnetize more readily than dipoles that can point in all directions. We also note that conventional mean-field theory makes no distinction between freely rotating dipoles and random axis Ising dipoles.

III. GENERALIZED MEAN-FIELD THEORY

When dipoles assume random positions, each dipole $\boldsymbol{\mu}_i$ feels a different field $\mathbf{H}_i$, giving rise to a thermal average $\langle \boldsymbol{\mu}_i \rangle_T$ which varies from dipole to dipole. Klien's theory[6,7] considers the probability distribution $P(\mathbf{H})$ of the field on any dipole, with mean $\mathbf{H}_0$ just as in conventional mean-field theory, and nonvanishing width δ (conventional mean-field states $\delta = 0$).

The thermal average $\langle \boldsymbol{\mu} \rangle$ captures only one aspect of the thermal state of an individual dipole. Instead, define the dipole orientation distribution $Q(\hat{\mu})$ which depends on the field distribution $P(\mathbf{H})$,

$$Q(\hat{\mu}) = \int d^3\mathbf{H}\, P(\mathbf{H}) \frac{e^{\beta\boldsymbol{\mu}\cdot\mathbf{H}}}{\sum_{\hat{\mu}} e^{\beta\boldsymbol{\mu}\cdot\mathbf{H}}} . \tag{15}$$

We express the long-range magnetic order parameter $\mathbf{M}$ in terms of $Q(\hat{\mu})$

$$\mathbf{M}=\rho\int d^2\hat{\mu}Q(\hat{\mu})\hat{\mu}\ . \tag{16}$$

This orientation distribution $Q(\hat{\mu})$ in turn determines the field distribution $P(\mathbf{H})$. In the following we derive this link in the self-consistency loop.

The field distribution $P(\mathbf{H})$ due to N randomly positioned particles

$$P(\mathbf{H})=\int\prod_{j=1}^{N}d^{3N}\mathbf{r}_j d^{2N}\hat{\mu}_j\mathcal{D}(\{\mathbf{r},\hat{\mu}\})\,\delta\left[\mathbf{H}-\sum_{j=1}^{N}\frac{1}{r_j^3}[3\hat{r}_j(\mu_j\cdot\hat{r}_j)-\mu_j]\right], \tag{17}$$

where $\mathcal{D}(\{\mathbf{r},\hat{\mu}\})$ is the probability distribution of the positions and dipole orientations of all dipoles from 1 to N. We decouple the probability distribution $\mathcal{D}(\{\mathbf{r},\hat{\mu}\})$ into single-particle distributions $D(\mathbf{r},\hat{\mu})$,

$$\mathcal{D}(\{\mathbf{r},\hat{\mu}\})\approx\prod_{j=1}^{N}D(\mathbf{r}_j,\hat{\mu}_j)\ . \tag{18}$$

This approximation simplifies the Fourier transform of the field distribution $P(\mathbf{H})$,

$$F(\mathbf{q})\equiv\int d^3\mathbf{H}P(\mathbf{H})e^{-i\mathbf{q}\cdot\mathbf{H}} \tag{19}$$

$$=\left[\int d^3\mathbf{r}\,d^2\hat{\mu}D(\mathbf{r},\hat{\mu})e^{-i(1/r^3)[3(\mathbf{q}\cdot\hat{r})(\mu\cdot\hat{r})-q\cdot\mu]}\right]^N. \tag{20}$$

Now rewrite Eq. (20) as

$$F(\mathbf{q})=\left[1-\int d^3\mathbf{r}\,d^2\hat{\mu}D(\mathbf{r},\hat{\mu})(1-e^{-i(1/r^3)[3(\mathbf{q}\cdot\hat{r})(\mu\cdot\hat{r})-q\cdot\mu]})\right]^N \tag{21}$$

and use the identity

$$\lim_{N\to\infty}\left[1-\frac{\mathcal{W}}{N}\right]^N=e^{-\mathcal{W}} \tag{22}$$

to obtain

$$F(\mathbf{q})=e^{-\mathcal{W}(\mathbf{q})}\ , \tag{23}$$

where

$$\mathcal{W}(\mathbf{q})\equiv(W_R+iW_I)=N\int d^3\mathbf{r}d^2\hat{\mu}D(\mathbf{r},\hat{\mu})(1-e^{-i(1/r^3)[3(\mathbf{q}\cdot\hat{r})(\mu\cdot\hat{r})-q\cdot\mu]})\ . \tag{24}$$

Next we decouple the spatial and orientational degrees of freedom in the single-particle distribution $D(\mathbf{r},\hat{\mu})$, and set

$$D(\mathbf{r},\hat{\mu})=\frac{1}{V}g(\mathbf{r})Q(\hat{\mu})\ , \tag{25}$$

where $g(\mathbf{r})$ is the positional pair correlation function given by (8). Now,

$$W_R(\mathbf{q})=\rho\int d^2\hat{\mu}\,Q(\hat{\mu})\int_{r>a}d^3\mathbf{r}\left\{1-\cos\left[\frac{1}{r^3}[3(\mathbf{q}\cdot\hat{r})(\mu\cdot\hat{r})-\mathbf{q}\cdot\hat{\mu}]\right]\right\}, \tag{26}$$

$$W_I(\mathbf{q})=\rho\int d^2\hat{\mu}\,Q(\hat{\mu})\int_{r>a}d^3\mathbf{r}\sin\left[\frac{1}{r^3}[3(\mathbf{q}\cdot\hat{r})(\mu\cdot\hat{r})-\mathbf{q}\cdot\mu]\right]. \tag{27}$$

Inverse Fourier transforming $F(\mathbf{q})$ yields

$$P(\mathbf{H})=\frac{1}{(2\pi)^3}\int d^3\mathbf{q}F(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{H}}$$

$$=\frac{1}{(2\pi)^3}\int d^3\mathbf{q}\,e^{i[\mathbf{q}\cdot\mathbf{H}-W_I(\mathbf{q})]-W_R(\mathbf{q})}\ . \tag{28}$$

Equations (15) for $Q(\hat{\mu})$ in terms of $P(\mathbf{H})$ and (28) for $P(\mathbf{H})$ in terms of $Q(\hat{\mu})$ constitute a self-consistent formulation for randomly positioned dipoles.

In calculating $P(\mathbf{H})$ from Eq. (28), the small-q region is most important, since the magnitude of the integrand $F(\mathbf{q})$ is close to a Gaussian for small q, and is exponentially small for large q. It is therefore sensible to expand $W_R(\mathbf{q})$ and $W_I(\mathbf{q})$ in powers of q. Equation (26) yields

$$W_R(\mathbf{q})=\frac{2\pi\rho\mu^2q^2}{15a^2}\int d^2\hat{\mu}Q(\hat{\mu})[3+(\hat{q}\cdot\hat{\mu})^2]$$

$$+O\left[\frac{\mu^4q^4}{a^9}\right], \tag{29}$$

which controls the shape and with of the field distribution $P(\mathbf{H})$. In the limit $a\to0$, $W_R(\mathbf{q})\propto q$, corresponding to a $P(\mathbf{H})$ of Lorentzian form consistent with Vugmeister and Glinchuk.[7] For finite a, however, $W_R(\mathbf{q})\propto q^2$ to

leading order, corresponding to $P(\mathbf{H})$ of Gaussian form with width

$$\delta \propto \sqrt{\rho\mu^2/a^3} \ . \tag{30}$$

The field distribution $P(\mathbf{H})$ has mean $\mathbf{H}_0=(4\pi/3)\mathbf{M}$ exactly as in conventional mean-field theory, dictated by Eq. (27) for

$$W_I(\mathbf{q})=\frac{4\pi}{3}\mu\mathbf{q}\cdot\mathbf{M}+O\left[\frac{\mu^3q^3}{a^6}\right] \ . \tag{31}$$

Conventional mean-field theory sets the spread $\delta=0$ and predicts ferromagnetic order for *all* densities at $T=0$. At the other extreme, Vugmeister and Glinchuk[7] consider randomly positioned *point* dipoles. Because the dipole-dipole interaction diverges rapidly for closely spaced pairs, the field distribution $P(\mathbf{H})$ is Lorentzian, with a spread proportional to the dipole density. Orientational order does not occur at *any* density, even at $T=0$.

Hard-sphere repulsion limits the closeness of dipoles, so the true field distribution $P(\mathbf{H})$ resembles a Gaussian with spread proportional to the square root of dipole density. The spread thus grows rapidly at small volume fraction ϕ, but more slowly for larger volume fraction. Our study shows that long-range orientational order emerges when the dipole volume fraction exceeds a certain critical value ϕ_c. We now explore this phenomenon in detail for several classes of random dipolar solid.

IV. FREELY ROTATING DIPOLES

In the absence of orientational order,

$$Q(\hat{\mu})=\frac{1}{4\pi} \tag{32}$$

and

$$W_R(\mathbf{q})=\frac{4\pi\rho\mu^2}{9a^3}q^2 \ . \tag{33}$$

The correction in $W_R(\mathbf{q})$ due to magnetic order is $\sim M^2$. An inverse Fourier transform [see Eq. (28) for $P(\mathbf{H})$ and Eq. (31) for $W_I(\mathbf{q})$] leads us to

$$P(\mathbf{H})=\frac{1}{(2\sqrt{\pi}\delta)^3}e^{-(\mathbf{H}-\mathbf{H}_0)^2/4\delta^2} \ , \tag{34}$$

where the Gaussian spread

$$\delta=\sqrt{4\pi\mu^2\rho/9a^3} \tag{35}$$

is isotropic plus anisotropic corrections of order H_0^2.

For any field $\mathbf{H}$, the thermal average

$$\langle\mu\rangle_T=\mu L(\beta\mu H)\hat{H} \ , \tag{36}$$

where

$$L(\beta\mu H)=\coth(\beta\mu H)-\frac{1}{\beta\mu H} \ , \tag{37}$$

is the well-known Langevin function. Averaging over fields yields the magnetic order parameter

$$\mathbf{M}=\rho\mu\int d^3\mathbf{H}\,P(\mathbf{H})L(\beta\mu H)\hat{H} \ . \tag{38}$$

For weak mean field $\mathbf{H}_0$ in the z direction, expanding (34) gives

$$P(\mathbf{H})=\frac{1}{(2\sqrt{\pi}\delta)^3}\left[1+\frac{H_0H_z}{2\delta^2}\right]e^{-H^2/4\delta^2} \ . \tag{39}$$

At the onset of magnetic order, self-consistency for mean field H_0 is

$$H_0=\frac{4\pi}{3}M$$
$$=\frac{4\pi}{3}\rho\mu\int d^3\mathbf{H}\,L(\beta\mu H)\frac{H_z}{H}\left[\frac{H_0H_z}{2\delta^2}\right]\frac{e^{-H^2/4\delta^2}}{(2\sqrt{\pi}\delta)^3} \ . \tag{40}$$

Let

$$y=\beta\mu H \tag{41}$$

and

$$\Delta=\beta\mu\delta=\sqrt{8\phi/3T^{*2}} \ . \tag{42}$$

The self-consistent condition (40) becomes

$$\int_0^\infty dy\,y^3L(y)e^{-y^2/4\Delta^2}=\frac{64}{3T^{*4}}\sqrt{2\pi\phi^3/3} \ . \tag{43}$$

Examine the high- and low-temperature limits of this condition: (i) High T^* corresponds to small Δ. The fast decaying Gaussian factor $e^{-y^2/4\Delta^2}$ means only the small-y regime contributes significantly to the integral. For small y,

$$L(y)\approx\frac{y}{3}-\frac{y^3}{45} \ , \tag{44}$$

giving the high-T^* phase boundary

$$T^*=\tfrac{8}{3}(\phi-\tfrac{1}{4}) \ , \tag{45}$$

where the constant term is a correction to the mean-field prediction [see Eq. (14)]. (ii) Low T^* corresponds to large Δ. The slowly decaying Gaussian factor $e^{-y^2/4\Delta^2}$ means the large-y regime contributes significantly to the integral. For large y,

$$L(y)\approx 1-\frac{1}{y} \ , \tag{46}$$

which gives the low-T^* phase boundary

$$T^*=\frac{32}{3\pi}\left[\phi-\frac{3\pi}{32}\right] \ . \tag{47}$$

At $T^*=0$, magnetic order persists for

$$\phi\geq\phi_c=\frac{3\pi}{32}\approx 0.295 \ . \tag{48}$$

Figure 1 shows the phase diagram of freely rotating dipoles over a range of temperature and volume fraction including the limits analyzed above.

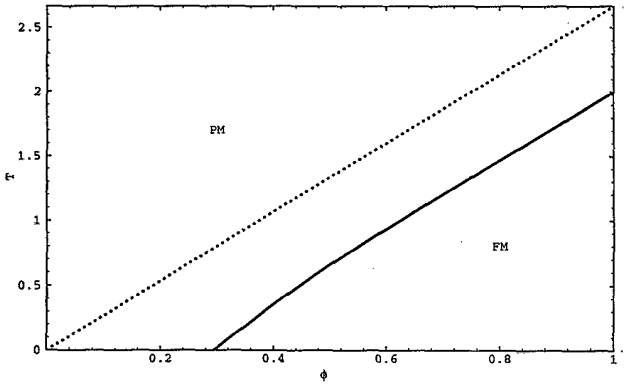

FIG. 1. Phase diagram for freely rotating dipoles. PM indicates paramagnet and FM indicates ferromagnet. The solid line is from generalized mean-field theory. The dotted line is conventional mean-field theory.

V. ISING DIPOLES

For Ising dipoles,

$$\hat{\mu}=\pm\hat{z} \ . \tag{49}$$

Equation (29) implies

$$W_R(\mathbf{q})=\frac{2\pi\rho\mu^2}{15a^3}(3q^2+q_z^2)$$
$$=\frac{2\pi\rho\mu^2}{15a^3}(3q_x^2+3q_y^2+4q_z^2) \tag{50}$$

independent of order parameter **M**. An inverse Fourier transform [see Eq. (28) for $P(\mathbf{H})$ and Eq. (31) for $W_I(\mathbf{q})$] gives the field distribution

$$P(\mathbf{H})=P_\perp(H_\perp)P_z(H_z) \ , \tag{51}$$

where $P_\perp(H_\perp)$ concerns the components in the xy plane,

$$P_\perp(H_\perp)=\frac{1}{4\pi\delta_\perp^2}e^{-H_\perp^2/4\delta_\perp^2}$$
$$=\frac{1}{4\pi\delta_\perp^2}e^{-(H_x^2+H_y^2)/4\delta_\perp^2} \tag{52}$$

and $P_z(H_z)$ concerns the z component,

$$P_z(H_z)=\frac{1}{2\sqrt{\pi}\delta_z}e^{-(H_z-H_0)^2/4\delta_z^2} \ . \tag{53}$$

The widths

$$\delta_\perp=\sqrt{2\pi\mu^2\rho/5a^3} \tag{54}$$

and

$$\delta_z=\sqrt{8\pi\mu^2\rho/15a^3} \ . \tag{55}$$

The mean field $H_0=(4\pi/3)M$ as in Eq. (7).

Ising dipoles point only in the $\pm\hat{z}$ directions. Following Eq. (15),

$$Q(\pm\hat{z})=\int_{-\infty}^{+\infty}dH_zP_z(H_z)\frac{e^{\pm\beta\mu H_z}}{2\cosh(\beta\mu H_z)} \ . \tag{56}$$

Note the order parameter

$$M=\rho\mu[Q(+\hat{z})-Q(-\hat{z})]$$
$$=\rho\mu\int_{-\infty}^{+\infty}dH_zP_z(H_z)\tanh(\beta\mu H_z) \ , \tag{57}$$

and the mean field

$$H_0=\frac{4\pi}{3}M=\frac{4\pi}{3}\rho\mu\int_{-\infty}^{+\infty}dH_zP_z(H_z)\tanh(\beta\mu H_z) \ . \tag{58}$$

The onset of magnetic order corresponds to small H_0, where

$$P_z(H_z)\approx\frac{1}{2\sqrt{\pi}\delta_z}\left[1+\frac{H_0H_z}{2\delta_z^2}\right]e^{-H_z^2/4\delta_z^2} \ . \tag{59}$$

Let

$$y=\beta\mu H_z \tag{60}$$

and

$$\Delta_z=\beta\mu\delta_z=\sqrt{16\phi/5T^{*2}} \ . \tag{61}$$

The self-consistent condition (58) becomes

$$\int_0^\infty dy y\tanh y e^{-y^2/4\Delta_z^2}=\frac{16}{5T^{*2}}\sqrt{\pi\phi/5} \ . \tag{62}$$

Examine the high- and low-temperature limits of this condition: (i) At high T^*, use

$$\tanh y\approx y-\frac{y^3}{3} \tag{63}$$

in the self-consistent equation (62) to yield the phase boundary for spontaneous magnetization:

$$T^*=8\phi-\tfrac{4}{5} \ . \tag{64}$$

The correction to conventional mean-field prediction [Eq. (12)] is a constant shift toward greater density. (ii) At low T^*, use

$$\tanh y\approx 1-2e^{-2y} \ , \tag{65}$$

yielding the low-temperature phase boundary for spontaneous magnetization

$$T^*=\sqrt{(64/5)(\phi-\pi/20)} \ . \tag{66}$$

At $T^*=0$, magnetic order persists for

$$\phi\geq\phi_c=\frac{\pi}{20}\approx 0.157 \ . \tag{67}$$

Figure 2 shows the complete phase diagram for Ising dipoles.

VI. RANDOM AXIS ISING DIPOLES

These dipoles point only along their easy axes which lie in all directions with equal probability. Therefore,

$$W_R(\mathbf{q})=\frac{4\pi\rho\mu^2}{9a^3}q^2 \ , \tag{68}$$

independent of magnetic order parameter **M**. The field distribution $P(\mathbf{H})$ has the same form as for freely rotat-

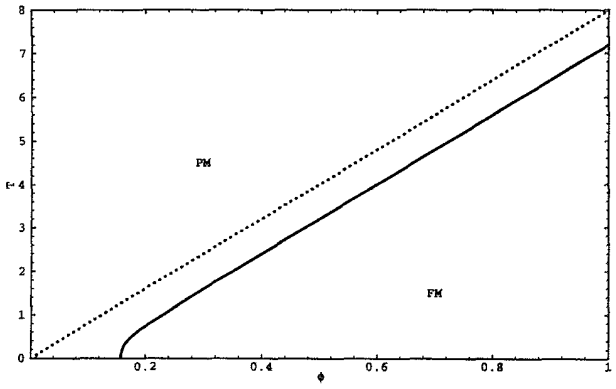

FIG. 2. Phase diagram for Ising dipoles. PM indicates paramagnet and FM indicates ferromagnet. The solid line is from generalized mean-field theory. The dotted line is from conventional mean-field theory.

ing dipoles [Eqs. (34) and (35)].

Relating $Q(\hat{\mu})$ to $P(\mathbf{H})$ by Eq. (15),

$$Q(\hat{\mu})=\frac{1}{2\pi}\int d^3\mathbf{H}\,P(\mathbf{H})\frac{e^{\beta\mu\cdot\mathbf{H}}}{e^{\beta\mu\cdot\mathbf{H}}+e^{-\beta\mu\cdot\mathbf{H}}} . \quad (69)$$

For magnetic order parameter $\mathbf{M}$ in the $+\hat{z}$ direction, Eq. (69) implies

$$M=\frac{\rho}{2\pi}\int d^3\mathbf{H}\,P(\mathbf{H})\int d^2\hat{\mu}(\mu\cdot\hat{z})\tanh(\beta\mu\cdot\mathbf{H}) . \quad (70)$$

At the onset of magnetic order, self-consistency for the mean field H_0 implies

$$1=\frac{2\pi\rho}{3\delta^2}\int d^3\mathbf{H}\,d^2\hat{\mu}\tanh(\beta\mu\cdot\mathbf{H})\frac{e^{-H^2/4\delta^2}}{(2\sqrt{\pi}\delta)^3}(\mathbf{H}\cdot\hat{z})(\mu\cdot\hat{z}) . \quad (71)$$

Note that the integral does not depend on $\hat{z}$. We can therefore make the substitution

$$(\mathbf{H}\cdot\hat{z})(\mu\cdot\hat{z})\rightarrow\tfrac{1}{3}\mu\cdot\mathbf{H} , \quad (72)$$

reached by averaging over all $\hat{z}$ directions holding the angle between μ and $\mathbf{H}$ fixed. Let

$$y=\beta\mu H , \quad (73)$$

$$\Delta=\beta\mu\delta=\sqrt{8\phi/3T^{*2}} , \quad (74)$$

$$x=\hat{\mu}\cdot\hat{H} . \quad (75)$$

The self-consistent equation becomes

$$\int_0^\infty dy y^3 e^{-y^2/4\Delta^2}\int_0^1 dx x\tanh(xy)=\frac{64}{3T^{*4}}\sqrt{2\pi\phi^3/3} . \quad (76)$$

The critical volume fraction at $T^*=0$ is

$$\phi_c(T^*=0)=\frac{3\pi}{8}\approx 1.18 . \quad (77)$$

At $T^*>0$,

$$\phi_c(T^*)>\phi_c(T^*=0)>1 . \quad (78)$$

Since, realistically, $\phi\leq 1$, spontaneous magnetization is forbidden in a system of random axis Ising dipoles.

VII. CONCLUSIONS

This paper studies spontaneous magnetic order in dipolar hard spheres having fixed, random positions. Conventional mean-field theory[10] describes a bulk continuum and neglects local fluctuations[13] due to dipole positional randomness, which tend to suppress magnetic order.[7] By incorporating a minimum dipole separation a, we establish the possibility of magnetic order in the presence of positional randomness for Ising dipoles and freely rotating dipoles at moderate and high volume fractions. At low volume fractions, the particle size becomes less relevant, the field distribution approaches a Lorentzian form, and the system should not magnetize even as $T\rightarrow 0$. We also study the effect of randomly oriented uniaxial anisotropy, finding that random axis Ising dipoles do not magnetize at realistic volume fractions ($\phi\leq 1$). In contrast, the conventional mean-field result does not differentiate between random axis Ising dipoles and freely rotating dipoles.

Several generalizations and improvements of our theory are possible. If the particles are aspherical, $g(\mathbf{r})$ becomes anisotropic at small $\mathbf{r}$. Among other things, this affects the mean field,[8] which is weaker for needle shapes and stronger for pancake shapes. For mobile dipoles, correlation between the $\mathbf{r}$ and $\hat{\mu}$ degrees of freedom may invalidate our separation of the two variables. While fine-tuning the pair correlation function may improve quantitative accuracy, our simple expression already suffices for qualitative insights. A serious deficiency of our theory is omission of the dipole glass state. It is expected that a replica analysis[9] will reveal a glassy state at low temperatures near our current ferromagnetic phase boundary.

We can compare our theory with results of some experiments. In the case of frozen ferrofluids, the particle easy directions are randomly oriented. At very low temperatures, competition between interparticle magnetic coupling and particle random anisotropy determines equilibrium magnetic ordering. Spherical particles having uniaxial crystalline anisotropy can be viewed as freely rotating dipoles if the ratio of anisotropy energy to dipole interaction energy is small, and as random axis Ising dipoles when the ratio is large. The magnetite particles in experiments[5] by Luo *et al.* have uniaxial anisotropy energy $\approx 1.5\times 10^{-15}$ erg and dipole energy at constant $\approx 4\times 10^{-13}$ erg, clearly in the limit of freely rotating dipoles. We note that these experiments[5] are conducted in the range $\phi\leq 0.233$, which falls in the regime where we predict no magnetization even in freely rotating dipoles. The absence of magnetic order they find is therefore consistent with our predictions. We hope these experiments can be repeated at higher volume fractions.

Our study assumes the system is in equilibrium. However, at low temperatures equilibration time may far exceed measurement time. In frozen ferrofluids, individual magnetic particles must overcome barriers of anisotropy energy while rotating their dipole moments (Néel re-

laxation). The Néel relaxation time[5]

$$\tau_N = \tau_0 e^{KV/k_B T}, \tag{79}$$

where $\tau_0 = 10^{-9}$ sec, and K and V are anisotropy constant and particle volume. The magnetite particles used in the frozen ferrofluid experiments[5] have diameter 50 Å and anisotropy constant $K \approx 2.3 \times 10^4$ ergs/cc. At $T = 4.5$ K, their Néel relaxation time $\tau_N \approx 1.0 \times 10^{-8}$ sec. Aside from anisotropy energy barriers in individual particles, interparticle interactions can also slow down equilibration. In the frozen ferrofluid experiments,[5] nonexponential decay of thermoremanent magnetization at $T = 15$ K yields a relaxation time of order 10^4 sec, far greater than the Néel relaxation time of individual particles. This indicates that collective effects are a chief source of the glassy behaviors observed in frozen ferrofluids.[5] We do not address the glassy phase.

Liquid dipolar fluids correspond to freely rotating dipoles. In the computer simulations of dipolar hard spheres[15,16] the lowest volume fraction for the magnetized phase was found at $\phi = 0.157$, $T^* = 0.0816$.[16] This point is outside the ferromagnetic region predicted by our study. Our study does not incorporates the effect of particle mobility, and therefore only sheds indirect light on the phase diagram of liquid ferrofluids. However, since particle mobility provides an additional degree of freedom to accommodate magnetic order, we believe liquid ferrofluids have a stronger tendency to spontaneously magnetize.

Experiments on randomly distributed Ising spins[1] yield a phase diagram in good agreement with our prediction, with a continuous phase boundary consistent with conventional mean field result at high and moderate temperatures and bending toward higher density at lower temperatures. The constant offset which our theory predicts [see Eq. (64)] vanishes when dipoles occupy random lattice sites rather than arbitrary positions in space. Again, the experiment observes a glassy phase at extremely low temperature, which we do not address.

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